solution was stirred at intervals and maintained at 60–70° for six hours, then poured into iced water. The mixture was extracted with benzene and the benzene extract washed with 10% hydrochloric acid, 10% sodium hydroxide, and finally with water. After removal of the benzene, the solid residue was recrystallized from aqueous alcohol to yield an amide which melted at 132–133°, the analytical sample. Other samples of this amide melted at 135–137° and 139–142°. *Anal.* Calcd. for $C_{12}H_{15}NO$: C, 76.15; H, 7.99. Found: C, 75.98; H, 8.27. The amide was probably a mixture of the anilide of cyclopentanecarboxylic acid (IV), m. p. 159–160°,[11] and N-cyclopentylbenzanilide, m. p. 157–158°.[12]

The amide was hydrolyzed with alcoholic hydrochloric acid to yield finally aniline and cyclopentanecarboxylic acid. The aniline was identified by its benzoyl derivative, m. p. 163.5–164.5° and mixed m. p. with an authentic sample of benzanilide 162.5–163.5°. The cyclopentanecarboxylic acid was converted to its anilide IV, m. p. 159–161°; mixed m. p. with an authentic sample of cyclopentanecarboxylic acid anilide, 161–162.5°.

Cyclopentanecarboxylic acid was synthesized from cyclopentylmagnesium bromide by carbonation and converted to the anilide IV, m. p. 162.5–163.5°, literature 159–160°.[11]

Synthesis of Cyclopentylphenylcarbinol II, and Cyclopentylphenyl Ketone III.—The carbinol was synthesized from 0.7 mole of benzaldehyde and 0.7 mole of cyclopentylmagnesium bromide[13]; yield 50 g. (40%); b. p. 110–112° (5 mm.); $n^{20}D$ 1.5412. *Anal.* Calcd. for $C_{12}H_{10}O$: C, 81.78; H, 9.15. Found: C, 81.80; H, 9.45.

The carbinol II was oxidized to cyclopentyl phenyl ketone III as described above; b. p. 100–108° (5 mm.); $n^{20}D$ 1.5422. The 2,4-dinitrophenylhydrazone melted at 144–144.5°. A mixture of this 2,4-dinitrophenylhydrazone and that of the ketone derived from the 2-phenylcyclohexylamine reaction melted at 144–145°.

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(11) Haworth and Perkin, *J. Chem. Soc.*, **65**, 100 (1894).

(12) Markownikow and Kaschirin, *Ber.*, **30**, 975 (1897).

(13) Edwards and Reid (THIS JOURNAL, **53**, 3234 (1930)) reported a synthesis of cyclopentylphenylcarbinol from cyclopentylmagnesium chloride and benzaldehyde in 7% yield. They give the boiling point as 129–131° (5 mm.) but state that their product was rather impure as indicated by their analyses.

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Synthesis of α-D-Glucose-1-phosphate and α-D-Galactose-1-phosphate

BY THEODORE POSTERNAK[1]

Until recently, the only method of synthesis of α-aldose-1-phosphates was the one devised by Cori, Colowick and Cori.[2,3] According to their procedure, an α-acetobromo-aldose is treated with trisilver phosphate. The condensation product, which seems to be composed mainly of a tertiary ester, is partially hydrolyzed with acid in order to remove two sugar residues, and then deacetylated. The over-all yield is poor because the reaction involves the loss of two-thirds of the starting sugar.

In the synthesis of α-D-glucose-1,6-diphosphate,[4] another procedure has been successfully used. It depends upon treating an α-acetobromo-aldose with silver diphenylphosphate. The phenyl groups are then removed from the condensation product by catalytic hydrogenation and the acetyl groups by alkali. Thus, an aldose-1-phosphate is formed which, in the case of glucose-1,6-diphosphate, is mainly the α-form.

The application of this new method to the synthesis of two biochemically important sugar phosphates, glucose-1-phosphate and galactose-1-phosphate, is described here. In these cases, again, the naturally occurring α-forms were obtained as the principal reaction products. It has already been pointed out[4] that silver diphenylphosphate differs markedly from other monosilver phosphate derivatives, in that it condenses with α-acetobromo sugars without inversion, while silver dibenzylphosphate[5] and "monosilver phosphate"[6] condense chiefly with inversion. In this work α-D-glucose-1-phosphate and α-D-galactose-1-phosphate were obtained as crystalline potassium salts, in 37% and 44% over-all yields, respectively. The best reported yields obtained by the trisilver phosphate procedure are one-fourth to one-sixth as large.[3,7]

Another method of preparing α-aldose-1-phosphates was also investigated. β-D-glucose-2,3,4,6-tetraacetate was dissolved in pyridine and left at room temperature. The final rotation indicated the presence of an equilibrium mixture containing about 20% of β- and 80% of α-D-glucose-2,3,4,6-tetraacetate. This solution was then treated with diphenyl chlorophosphonate. After the removal of the phenyl groups by catalytic hydrogenation and deacetylation with alkali, α-D-glucose-1-phosphate was isolated as the crystalline potassium salt. However, the over-all yield (10%) was much lower than by the first new procedure.

Grateful acknowledgment is expressed to Prof. C. F. Cori for his interest in this work.

Experimental

Barium α-D-Glucose-1-phosphate and Barium α-D-Galactose-1-phosphate.—A solution of 0.6 g. (0.00146 mole) of α-acetobromoglucose or of α-acetobromogalactose was prepared in 2 ml. of dry benzene. After the addition of 0.52 g. (0.00146 mole) of dry, finely powdered silver diphenylphosphate,[4] the mixture was refluxed for half an hour with exclusion of moisture. Then 0.25 g. of silver diphenylphosphate was added and the mixture was refluxed again for half an hour. After centrifugation and thorough washing of the silver salts with dry benzene, the solvent was evaporated under reduced pressure. The residue was dried *in vacuo*, and then dissolved in 8 ml. of absolute ethanol. The filtered solution was exhaustively hydrogenated at room temperature and atmospheric pressure in the presence of 100 mg. of platinic oxide.

For the deacetylation of the glucose derivative, 1 *M* sodium hydroxide was added dropwise until a permanent pink color was obtained with phenolphthalein. However, the deacetylation of the galactose derivative had to be carried out under more drastic conditions: following the

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(2) (a) C. F. Cori, S. P. Colowick and G. T. Cori, *J. Biol. Chem.*, **121**, 465 (1937); (b) S. P. Colowick, *J. Biol. Chem.*, **124**, 557 (1938).

(3) M. E. Krahl and C. F. Cori in "Biochemical Preparations," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1949.

(4) T. Posternak, *J. Biol. Chem.*, **180**, 1269 (1949).

(5) M. L. Wolfrom, C. S. Smith, D. E. Pletcher and A. E. Brown, THIS JOURNAL, **64**, 23 (1942).

(6) F. J. Reithel, *ibid.*, **67**, 1056 (1945).

(7) H. W. Kosterlitz, *Biochem. J.*, **33**, 1087 (1939).

hydrogenation, 1.0 ml. of 10 *M* sodium hydroxide was added and the mixture was heated to boiling for three minutes; after cooling, it was neutralized with glacial acetic acid.

After the deacetylation, ethanol was removed by distillation *in vacuo* and a concentrated aqueous solution of 500 mg. of barium acetate was added. An insoluble precipitate was removed by centrifugation and washed with water. By the addition of 8 volumes of ethanol to the combined water solutions, the barium aldose-1-phosphate was precipitated. It was filtered and washed with ethanol and ethyl ether.

Potassium α-D-Glucose-1-phosphate.—The barium glucose-1-phosphate obtained (350 mg.) was dissolved in water. The solution was filtered and 155 mg. of potassium sulfate was added. The barium sulfate was removed by centrifugation. By the dropwise addition of 1.5 volumes of ethanol at 0°, potassium glucose-1-phosphate precipitated as fine needles (200 mg.). For analysis the product was recrystallized in the same manner, $[\alpha]^{25}D$ +78 ± 1° (c = 0.81, water).[8]

Anal. Calcd. for $C_6H_{11}O_9PK_2 \cdot 2H_2O$: total P, 8.33; labile P, 8.33. Found: total P, 8.16; labile P, 8.12.[10]

The α-glucose-1-phosphate sample obtained by this procedure was converted enzymatically by phosphoglucomutase to the same equilibrium mixture (containing 95% glucose-6-phosphate) as is the naturally occurring 1-ester.[11]

Potassium α-D-Galactose-1-phosphate.—The barium salt obtained (560 mg.) contained: total P, 6.54; labile P, 6.50.

Since the potassium salt of galactose-1-phosphate did not crystallize without seeding, the substance was at first purified as the crystalline brucine salt. To a water solution of 480 mg. of the barium salt 1 g. of brucine sulfate was added. The suspension was heated; barium sulfate was removed by centrifugation from the hot mixture and was washed with hot water. The combined supernatant fluids were concentrated *in vacuo* to 5 ml. Upon the addition of 15 ml. of acetone, the brucine salt crystallized (900 mg.). This salt was suspended in 3 ml. of water and 10% potassium hydroxide was added until a permanent pink color was obtained with phenolphthalein. Brucine was removed by exhaustive extraction with chloroform. During slow addition of ethanol at 0°, potassium α-D-galactose-1-phosphate crystallized in fine needles (240 mg.); $[\alpha]^{32}D$ +100 ± 1° (c = 1.57, water).[12]

Anal. Calcd. for $C_6H_{11}O_9PK_2 \cdot 2H_2O$: total P, 8.33; labile P, 8.33. Found: total P, 8.26; labile P, 8.22.

In another experiment, 490 mg. of the barium salt was treated directly with potassium sulfate in the usual manner for transformation into the potassium salt. The latter salt crystallized upon seeding (295 mg.); it was analytically pure after two recrystallizations (220 mg.).

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(8) The rotation reported by Wolfrom, *et al.*,[9] is $[\alpha]^{20}D$ +78°.

(9) M. L. Wolfrom and D. E. Pletcher, THIS JOURNAL, **63**, 1050 (1941).

(10) Labile P was determined as the amount of inorganic P formed during ten minutes of hydrolysis in 1 *N* HCl at 100°.

(11) This experiment was carried out by Dr. E. W. Sutherland.

(12) The rotation indicated by Kosterlitz[7] is $[\alpha]^{18}D$ +98°.

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Vapor Density of Diborane

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It is of interest to compare data on unusual compounds with generalized correlations based largely on hydrocarbons and their derivatives. Such a comparison is afforded by recent vapor density data on diborane by Smith and Miller[1] which may be compared with generalized *P–V–T* relations.[2,3,4] These have been found to be a fair approximation for hydrocarbons and a number of other substances (A, Ne, H_2, N_2, He, Kr, O_2,

TABLE I

VAPOR DENSITY OF DIBORANE (UNSATURATED VAPOR)

Temp.,[a] °K.	Pressure, p. s. i. a.	Density, g./cc.	T_R	P_R	$z = PV/RT$ Obsd.[1]	Gen.[b]	Berth.[c]
243.6	85	0.00873	0.841	0.145	0.92	0.89	..
243.6	131	.0148	.841	.224	.83	.83	0.86
243.6	172	.0332	.841	.294	.49[d]	.77	.82
243.6	173	.0392	.841	.295	.42[d]	.77	..
250.0	57	.00522	.864	.097	1.00	.94	..
250.0	71	.00669	.864	.121	0.97	.92	..
250.0	125	.0133	.864	.213	.86	.86	..
250.0	178	.0220	.864	.304	.74	.79	..
250.0	183	.0214	.864	.312	.78	.78	..
250.0	208	.0397	.864	.355	.48[d]	.75	..
256.1	64	.00583	.885	.109	0.98	.93	..
256.1	68	.00610	.885	.116	1.00	.93	..
256.1	131	.0136	.885	.224	0.86	.86	.88
256.1	198	.0232	.885	.338	.77	.77	..
256.1	243	.0359	.885	.415	.61[d]	.71	.78
268.1	109	.00943	.926	.186	.99	.90	..
268.1	181	.0187	.926	.309	.83	.83	..
268.1	276	.0326	.926	.471	.72	.72	..
268.1	324	.0427	.926	.553	.65	.65	..
277.8	118	.0108	.960	.201	.90	.91	..
277.8	153	.0138	.960	.261	.92	.88	..
277.8	298	.0345	.960	.509	.71	.74	..
277.8	420	.0604	.960	.717	.58	.58	..

[a] Data at 284.1, 287.1 and 292.5°K. are not shown since generalized correlations are not considered to be reliable at such high values of T_R (0.981, 0.992, 1.010). [b] Generalized *P–V–T* correlation.[2,3] [c] Berthelot equation. [d] These points show greatest divergence from generalized correlation but agree with data on the saturated gas.

TABLE II

VAPOR DENSITY OF DIBORANE (SATURATED VAPOR)

Temp., °K.	Pressure,[a] mm.	Density, g./cc.	T_R	P_R	$z = PV/RT$ Obsd.[1]	Gen.[b]
207.0	2531	0.0151	0.715	0.0836	0.36	0.91
215.5	3569	.0145	.744	.118	.51	.88
227.9	5626	.0673	.787	.186	.16	.83
235.4	7238	.0348	.813	.239	.39	.79
240.3	8461	.0407	.830	.279	.38	.77
246.2	10130	.0382	.850	.335	.48	.74
251.3	11750	.0393	.868	.388	.53	.71
255.3	13150	.0470	.882	.434	.49	.69
260.8	15260	.0492	.901	.504	.53	.66
265.8	17370	.0541	.918	.574	.54	.62
269.9	19260	.0567	.932	.636	.56	.59
270.7	19640	.0588	.935	.649	.55	.59
274.0	21290	.0625	.946	.703	.55	.56
278.9	23890	.0581	.963	.789	.66	.52
283.0	26240	.0759	.978	.867	.54	.47
285.2	27560	.0927	.985	.910	.46	.45
286.2	28180	.0950	.989	.931	.46	.40
288.2	29430	.1100	.996	.972	.41	.40

[a] Calculated from vapor pressure equation. [b] Generalized *P–V–T* correlation.[2,3]

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(1) S. H. Smith, Jr., and R. R. Miller, THIS JOURNAL, **72**, 1452 (1950).

(2) J. Q. Cope, W. K. Lewis and H. C. Weber, *Ind. Eng. Chem.*, **23**, 887 (1931).

(3) G. W. Thomson, *ibid.*, **35**, 895 (1943).

(4) R. H. Newton, *ibid.*, **27**, 302 (1935).